EXPERIMENTAL STUDIES OF ELECTRON BINDING ENERGIES AND AUGER SPECTRA

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INAUGURAL DISSERTATION

BY

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Experimental Studies of Electron Binding Energies and Auger Spectra

Binding energies of the inner electrons of atoms have almost exclusively been studied by the method of X-ray absorption. During the 1920's and 1930's the K and L absorption spectra were investigated for the majority of elements in the periodic system, and the M absorption spectra were studied for the heavier elements. Complete energy-level systems were calculated from the energies of absorption limits and emission lines. Consequently, our present knowledge of the energy levels in atoms has been gathered almost solely from X-ray spectroscopy.

A different approach to the problem of determining electron binding energies was made by H. R. Robinson and his collaborators as early as 1914. Part of the absorption of X-rays is due to a photo-electric effect and it should be possible to observe the photo electrons expelled from the various shells of an atom. Moreover, Einstein's photo-electric law should be applicable to the photo-electron energies. In Robinson's experiments the photo electrons expelled by X-radiation of a given frequency ($K\alpha$ radiation) were analyzed in a semicircular magnetic spectrograph. The results of these measurements were in good agreement with the data of X-ray spectroscopy, but the precision of the photo-electron method was never brought to its inherent limits.

The present thesis reports a further development of the photo-electron method to a precision range which is about a hundred times higher than that obtained previously. This high precision has also made possible studies of the energy shifts of inner electronic levels due to oxidation and alloying, and the photo-electron method must now be considered a valuable complement to the X-ray absorption method for the study of inner electron levels. The energies measured by the photo electron method are obtained from electron *lines* and are always determined relative to the Fermi level of the solid, whereas the shape and energy of an absorption *edge* depend on the density of states in the outer bands and selection rules governing the absorption process. Thus, the photo electron spectrum gives information primarily on the inner atomic levels, and the X-ray absorption spectrum elucidates the structure of the outer bands of the solid. However, much effort has been made to give a correct interpretation of X-ray absorption spectra, and it is of great interest to compare the results obtained by the two methods.

The inner vacancy created in the photo-electric process is filled by an electron from an outer shell, with the simultaneous emission of a photon. A competing process is non-radiative transition. Here the transition energy is delivered to an orbital electron which is ejected from the atom. These so-called Auger electrons give rise to complicated spectra which can be studied in detail only with instruments of very high resolution. Experimental studies of Auger spectra are reported in two of the papers.

The thesis is based on investigations published in the following six papers:

I. Evelyn Sokolowski, Carl Nordling and Kai Siegbahn: Magnetic analysis of X-ray produced photo and Auger electrons. *Arkiv för Fysik 12*, 301–318 (1957).

II. Evelyn Sokolowski and Carl Nordling: Experimental studies of the *KLL* Auger spectra of Cu and Ge. *Arkiv för Fysik 14*, 557–564 (1959).

III. Carl Nordling, Evelyn Sokolowski and Kai Siegbahn: Evidence of chemical shifts of the inner electronic levels in a metal relative to its oxides. (Cu, Cu_2O, CuO). *Arkiv för Fysik 13*, 483–500 (1958).

IV. Carl Nordling: Energy shifts of *L*-levels in some 5th period elements due to oxidation and alloying. *Arkiv för Fysik 15*, 241–250 (1959).

V. Carl Nordling: *K* and *L* energy levels in some fourth and fifth period elements. *Arkiv för Fysik 15*, 397–429 (1959).

VI. Carl Nordling and Stig Hagström: Electron binding energies in uranium. *Arkiv för Fysik 15*, 431–443 (1959).

The experimental arrangements are described in *Paper I*, which also reports some measurements of the electron spectra obtained from metallic copper. Preliminary values are given for the *K* and L_I binding energies as well as *KLL* and *KLM* Auger line energies.

Recently, Asaad and Burhop have calculated the energies and intensities of the *KLL* and *KLM* Auger lines for different atomic numbers, using a non-relativistic theory based on an intermediate coupling between the two inner shell vacancies of the final state. The energies of the Auger lines of copper and germanium, belonging to the *KLL* group, are determined experimentally in *Paper II*, and the intensities are estimated. Good agreement is found between the experimental data and the theoretical results of Asaad and Burhop, as regards the relative energies and intensities. The absolute line positions are found to deviate by about 50 eV from the calculated values.

Energy shifts of the *K* and *L* levels of copper due to oxidation are studied in *Paper III*. In all cases a shift is observed towards greater binding energy on going from the metal to the oxide. The greatest shift is observed for the *K* and L_I levels in the cupric oxide. The shift of the *K* binding energy for CuO is correlated to investigations on the band structure of the oxide. Indications are found of changes in the level widths due to oxidation. A shift towards lower energy in CuO is observed for the strongest line in the *KLL* Auger spectrum. Also, there is some evidence that the *K* Auger yield depends on the chemical composition of the source.

In *Paper IV* the effects of oxidation and alloying on L levels in cadmium and tin are investigated. The L_{I} and L_{III} energies of Cd are found to be lower in the oxide than in the metal. Conversely, in the oxides SnO and SnO_2 the L energies of tin are around 1 eV higher than in the metal. No shift is observed in the SnAu alloy. Infinitely thick as well as thin converters are used.

In *Paper V* the photo electron method is applied to a study of K and L binding energies in the fourth period and L binding energies in the fifth period of the periodic table. Calibration lines are obtained from "absolute" $B\varrho$ determinations and the errors inherent in this calibration method are discussed for non-relativistic electron energies. The results of the subsequent energy determinations are given in modified Moseley diagrams together with representative X-ray data. Certain discrepancies are observed between the energies obtained with the photo-electron method and those determined by the conventional X-ray absorption method.

Paper VI reports the application of the photo electron method to an element in the last period, viz. uranium. Altogether ten energies in the L, M and N shells are measured with an accuracy of a few tenths of an electron volt. Only a minority of the corresponding X-ray absorption edges have been observed. Energy values of the K and L levels are deduced by adding energies of X-ray transitions to M and N binding energies obtained by the photo electron method. Comparisons are made between the results of this method and those of X-ray spectroscopy, and an observed discrepancy for the L_{III} energy is discussed.

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Uppsala, April 1959. *Carl Nordling*